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(54) Title: FAMILY OF MONOMERIC, REACTIVE, AND POLYMERIC BENZOTRIAZOLES (57) Abstract Novel benzotriazoles (BZT) compounds are disclosed which are useful as high temperature stable monomeric benzotriazoles, polymerizable benzotriazoles, and polymers containing the benzotriazole functionality useful as ultraviolet light stabilizers, metal chelaters. Products of the present invention are derivatives of 4-hydroxyacetophenone benzotriazole (4-HAP-BZT), and 4-hydroxyphenylmethyl carbinol benzotriazole (4-HPMC-BZT).		

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A FAMILY OF MONOMERIC, REACTIVE, AND POLYMERIC BENZOTRIAZOLES

FIELD OF THE INVENTION

This invention relates to novel benzotriazoles (BZT's) useful as high temperature
5 stable, reactive or polymeric ultraviolet (UV) light absorbers/stabilizers (UVLS). The invention further relates to a family of novel BZT's particularly useful in a range of monomeric, reactive, and polymeric forms. Reactive BZT's can be incorporated directly into a polymer backbone while monomeric and polymeric forms can be used as polymer additives.

BACKGROUND OF THE INVENTION

10 As used herein, the term absorber refers to a compound that absorbs ultraviolet light generally in the wavelength range from 330 to 400 nanometers (nm). Thus absorbed, UV light cannot then lead to formation of free radicals which will result in polymer degradation.

"Light absorber" and "light stabilizer" are used interchangeably. Strictly speaking, a
15 "light absorber" literally absorbs UV radiation which reduces or eliminates light absorbed by polymer chromophores. A "light stabilizer" may absorb UV radiation, but it may also stabilize a polymer by reacting with or "scavenging" free radicals that are a result of light interaction with a polymeric material, causing the polymer to undergo photodegradation.

Additives to impart UV stabilizing properties or antioxidant properties to polymers or
20 to perform as colorants are known (US 5,438,142). Such additives generally are low molecular weight species, and have several problems including poor compatibility with the polymer matrix, poor dispersion into the polymer formulation, migration within the polymer, losses due to volatility of the additive material during processing or use, and leaching into liquids, for instance, when fabrics made of stabilized polymeric fibers are washed.

25 One method of overcoming these problems is to incorporate the stabilizer directly into the polymer; for example, nitroso compounds are directly incorporated into synthetic rubbers, while amine and phenol antioxidants have been grafted onto synthetic elastomers to form masterbatch concentrates which are subsequently blended with pure polymer.

It is known in the art that benzotriazoles (BZT's) and their derivatives, in particular 2-
30 (2'-hydroxyphenyl)-benzotriazoles, are useful as UV light absorbers and stabilizers. BZT's are able to eliminate excitation energy through proton transfer, thus preventing damage to the polymer backbone. "Oxidation Inhibition in Organic Materials", J. Psopisil, P. Klemchuk, Vol.

II, CRC Press, Inc., 1990, pp 40-43. Increased attention has been directed recently to the preparation of high temperature stabilizers. These may take the form of (1) high temperature stable BZT monomers suitable for use with high temperature thermoplastics without concern for blooming or flashing during processing, (2) monomers that contain a reactive group that can be reacted into a particular polymer backbone thus becoming part of the polymer itself (such as a vinyl group attached to an aromatic ring containing the ortho -OH and BZT functionality, said reactive (vinyl, but not limited to vinyl) group being reactive either for homopolymerization, or copolymerization with other suitable reactive monomeric compounds.

Vogl and Nir report the synthesis of several BZT compounds in US Patent A6537219, herein incorporated by reference in its entirety. Disclosed therein are new and known BZT UV light stabilizers, a process to synthesize same, and more particularly synthesis of the novel 2(2-hydroxy-5-isopropenylphenyl)2H-BZT. The process according to the Vogl et. al. invention comprises the azo coupling of o-nitrophenyl diazonium chloride with p-hydroxy-acetophenone. A series of reaction steps are involved to yield the desired 2(2-hydroxy-5-isopropenylphenyl)2H-BZT product.

The art is always searching for viable, preferably commercially suitable, synthetic routes for BZT compounds and starting materials that lend themselves to further derivatization to form higher temperature stable, more compatible end products or homopolymerization or copolymerization with other suitable monomers. Since polymers are, by nature, generally more temperature stable than monomeric BZT molecules, BZT compounds that lend themselves to polymerization, or reaction with other polymers may be particularly useful toward reaching higher temperature stable light absorbers.

SUMMARY OF THE INVENTION

The present invention relates to substituted (or functionalized) multi-aryl compounds useful for incorporation into polymers. The functionalized compounds are useful as components for UV light stabilizers/absorbers, antioxidants, and metal chelaters.

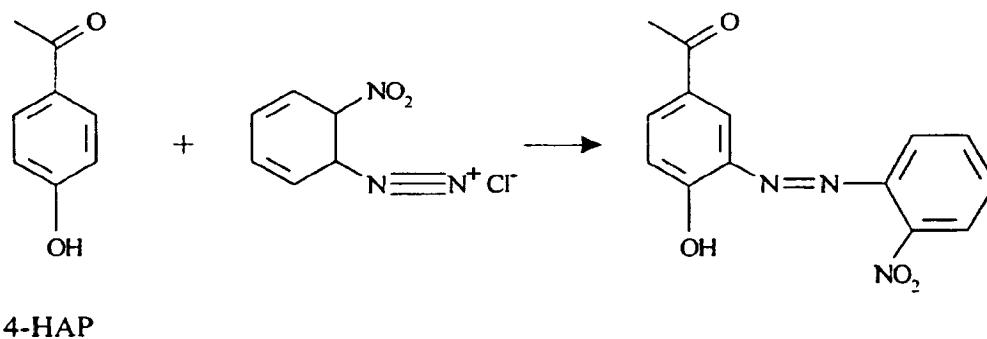
The present invention more particularly relates to BZT Light Absorbers which help stabilize polymers against degradation caused by ultraviolet light and comprises a family of unique BZT derivatives that lend themselves to further derivatization or homo or co, ter, etc. polymerization by themselves or with other monomers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

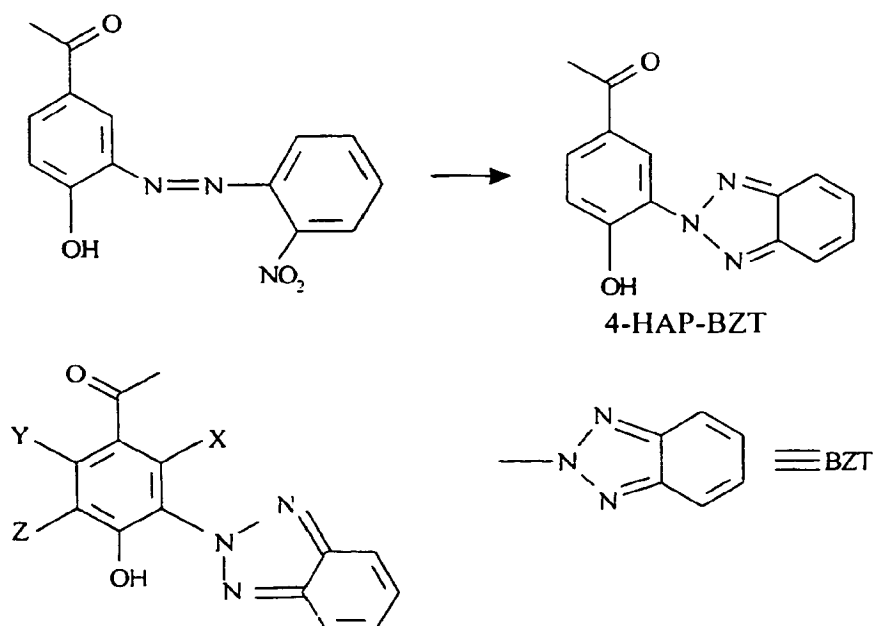
Novel benzotriazoles (BZT) compounds are disclosed which are useful high temperature stable monomeric benzotriazoles, polymerizable or reactive benzotriazoles, and polymers containing the benzotriazole functionality useful as ultraviolet light stabilizers.

Products of the present invention are derivatives of 4-hydroxyacetophenone benzotriazole (4-HAP-BZT), and 4-hydroxyphenylmethyl carbinol benzotriazole (4-HPMC-BZT); which is derived from 4-HAP-BZT.

One may practice the general invention by synthesizing the parent molecule 4-HAP-BZT or 4-HPMC-BZT or their respective adducts. 4-HAP-BZT is obtained through azo coupling to 4-hydroxyacetophenone



with subsequent reductive cyclization to the benzotriazole derivative



where X, Y, and Z are independently hydrogen, C₁ through C₂₀ carbon atom group, halogen or primary, secondary, or tertiary alkyl moieties.

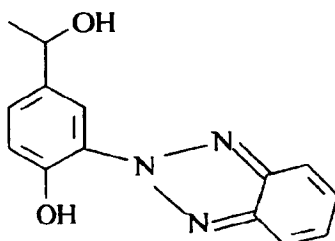
5 The invention will be described further in terms of various representative compositions. While the examples may illustrate the synthesis of 4-HAP-BZT or 4-HPMC-BZT derivatives, it is to be understood that where appropriate, similar derivatives with the foregoing formulas may be prepared by following similar procedures.

10 Suitable compounds may be homopolymerized or copolymerized via but not limited to condensation, free radical, ionic, solution, or suspension polymerization routes.

15 4-HAP-BZT is produced by the reaction of 4-hydroxyacetophenone (4-HAP) with the diazonium chloride salt of o-nitroaniline, forming the subsequent azo dye. This dye is subjected to reductive cyclization to form the benzotriazole. Reduction is achieved either chemically using a variety of reducing agents (such as thiourea dioxide), or catalytically using Raney nickel or any number of specialty supported precious metal on carbon catalysts. The resulting 4-HAP-BZT is further reduced to the secondary alcohol, using a variety of chemical reducing agents including, but not limited to NaBH₄, or by catalytic reduction using various catalysts, including, but not limited to Raney nickel, or supported precious metal on carbon under hydrogen pressure from about 50 psig to 2000 psig. 4-Hydroxyphenylmethyl carbinol Benzotriazole (4-HPMC-BZT) can
20 also be prepared directly from the azo dye via catalytic reduction by varying conditions of temperature and pressure. The resulting 4-HPMC-BZT is derivatized using a number of standard organic chemistries, described herein and in the art to yield a family of products of wide diversity, high temperature stability, and broad compatibility with many monomer and resin systems.

25 4-HAP-BZT can be subjected to a number of chemistries, including, but not limited to oximation, alkylation, reductive amination, and hydrogenation. The preferred process involves hydrogenation employing precious metal (i.e., Pd on carbon), Raney nickel, or NaBH₄ catalysts represented by the molecule 4-Hydroxyphenylmethyl carbinol Benzotriazole (4-HPMC-BZT):

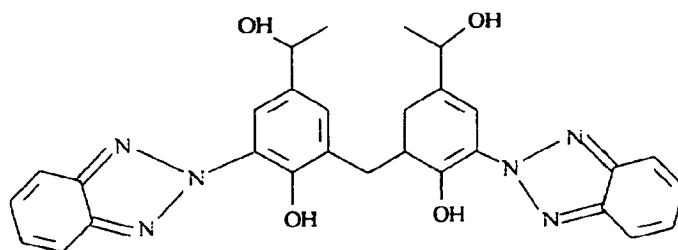
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4-HPMC-BZT

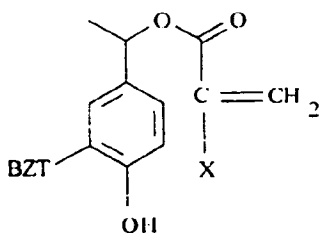
4-HAP-BZT and 4-HPMC-BZT are known in the literature. The present invention relates, in one embodiment, to novel chemistry to prepare each compound, and in another embodiment, to preparation of a class of derivative products of 4-hydroxyphenylmethyl carbinol, or 4-hydroxyacetophenone BZT.

Bis-hydroxyphenylmethyl carbinol benzotriazole (bis-HPMC-BZT), represented below,



bis-HPMC-BZT

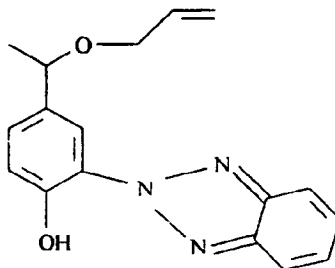
may be prepared by formaldehyde condensation of 2 moles of 4-HPMC-BZT by condensation and processing routes known to those of skill in the art. The following BZT-acrylate monomer may be employed in further polymerization.



wherein X is H, C₁ through C₂₀ alkyl, CN. The monomer may be produced via esterification of 4-HPMC with the appropriate acrylic or alkylacrylic acid or corresponding acid chloride under typical esterification conditions in the presence of an inhibitor to prevent polymerization of the

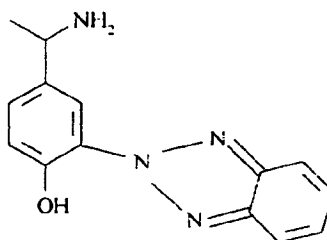
monomer.

4-HPMC Allylether Benzotriazole (4-HPMCAE-BZT) is represented below:



The monomer for 4-HPMCAE-BZT is produced through reaction of 4-HPMC-BZT with allyl alcohol under acidic conditions. Reaction gives high yields of a white solid.

Alpha-aminoethyl phenol benzotriazole (AEP-BZT).



may be produced via the reductive amination of 4-HAP-BZT under pressure using Raney nickel or Pd on carbon or other precious metal catalyst. The amine may be reacted with isocyanates to produce UV stable polyurethanes.

Thus, given the "parent" benzotriazole molecule, literally dozens of additional derivative materials, either monomeric, reactive, or polymeric may be synthesized. Owing to their functionality and reactivity, many of these derivatives find end use for improved performance in a variety of applications and polymer systems.

During polymerization and/or processing of polymers (e.g. polyesters), 4-HPMC-BZT can undergo reaction and become permanently fixed to the polymer chain. Incorporation of 4-HPMC-BZT into various polymers can eliminate problems with losses of stabilizing additives during processing and use.

PHS-BZT is a polymeric benzotriazole which we envision can be used as a UV absorber and stabilizer in polymers. Stabilization of the polymer matrix occurs by absorption of UV light, followed by deactivation of the energy associated with the light absorption through

proton transfer.

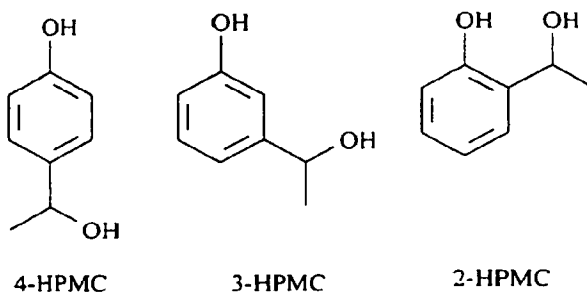
The above described embodiments, particularly the polymer bound stabilizers may also be used in applications relating to coatings, packaging, and textiles.

The following non-limiting examples are provided to illustrate the invention. The invention has been described with reference to its preferred embodiments. Those of ordinary skill in the art may, upon reading this disclosure, appreciate changes or modifications which do not depart from the scope or spirit of the invention as described herein.

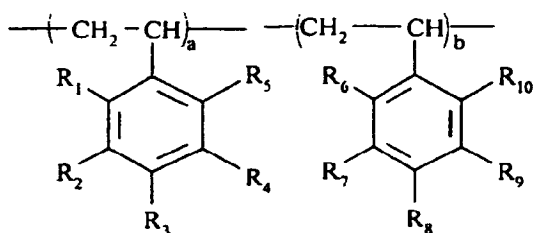
EXAMPLES

Poly(Hydroxystyrene Benzotriazole) (PHS-BZT)

A number of variations of poly(hydroxystyrene benzotriazole) (PHS-BZT) are produced through the homo-polymerization of 4-HPMC-BZT or polymerization with co-monomers such as ortho, meta, or para hydroxyphenylmethyl carbinol (2-HPMC, 3-HPMC or 4-HPMC). These polymers are synthesized in a melt or solution (e.g., methanol, acetic acid) polymerization using acid catalysts such as phosphoric, sulfuric, or hydrochloric acid. Graft polymers of PHS-BZT are synthesized in similar fashion where, for example, PHS is dissolved in acetic acid with 4-HPMC-BZT using sulfuric acid as a catalyst



PHS-BZT has the following general structure where R groups vary according to monomers used in the polymerization and "a" and "b" represent varying chain length in the polymer backbone:



wherein a, b = 1 - 1000.

The following examples are relative to PHS-BZT polymers:

(A) Homo polymer (4-HPMC-BZT monomer):

$R_1, R_4 = H$;

$R_3, R_8 = OH$;

$R_2, R_9 = BZT$.

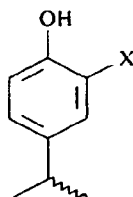
(B) Copolymer (4-HPMC + 4-HPMC-BZT):

$R_1, R_5, R_6, R_{10} = H$; $R_3, R_8 = OH$;

$R_2, R_4, R_7 = H$ or hydroxyphenylethane;

$R_9 = BZT$,

where hydroxyphenylethane is represented as:



wherein X may be H, hydroxylphenyl ethane, hydroxylphenyl ethane BZT, or BZT.

(C) PHS-BZT graft polymer: $R_1, R_4 = H$;

$R_2 = H$ or hydroxylphenyl ethane;

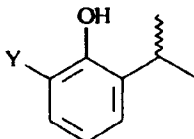
$R_3, R_6 = OH$;

$R_5 = \text{hydroxyphenylethane benzotriazole}$.

The following examples employ 2-HPMC as monomer:

(D) A copolymer of 4-HPMC-BZT and o-hydroxyphenylmethyl carbinol (2-HPMC +

4-HPMC-BZT) may contain the following ortho hydroxyphenylethane branch group:



wherein Y = H, o-hydroxyphenylethane, hydroxyphenylethane BZT;

R₁₋₆ are as identified in (B) above:

(E) A graft polymer of o-polyhydroxystyrene (o-PHS) and 4-HPMC-BZT:

R₁, R₄ = OH;

R₂ = H or o-hydroxyphenylethane;

R₃, R₆ = H;

R₅ = hydroxyphenylethane benzotriazole.

(F) o-PHS-BZT co-polymer (4-HPMC-BZT + 2-HPMC):

R₁, R₆ = OH;

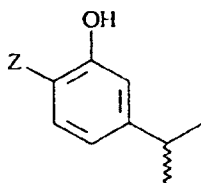
R₃, R₄ = H.

R₂ = H or o-hydroxyphenylethane or hydroxyphenylethane benzotriazole;

R₅ = benzotriazole

The following examples employ 3-HPMC as monomer:

(G) A co-polymer of m-hydroxyphenylmethylethanol (3-HPMC) and 4-HPMC-BZT would contain the following meta hydroxyphenylethane branch group:



m-hydroxyphenylethane branch wherein Z = H. or

m-hydroxyphenylethane, or

hydroxyphenylethane benzotriazole

(H) m-PHS-BZT graft polymer (4-HPMC-BZT + m-PHS):

R₃ = H or m-hydroxyphenylethane:

R₂, R₅ = OH;

$R_1, R_4 = H$;

$R_6 = \text{hydroxyphenylethane benzotriazole.}$

(I) m-PHS-BZT co-polymer (HPMC-BZT + 3-HPMC):

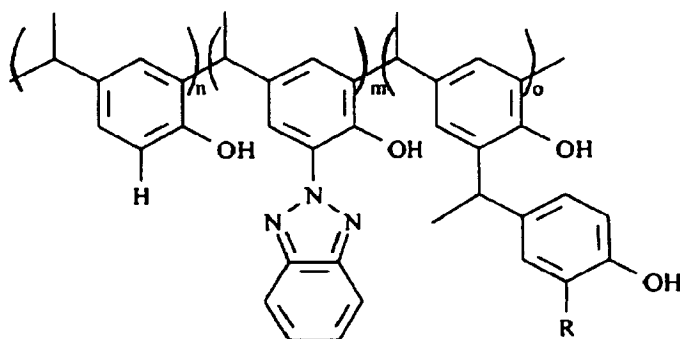
$R_1, R_4 = H$;

$R_2, R_6 = OH$;

$R_3 = H$ or hydroxyphenyl ethane benzotriazole or m-hydroxyphenylethane;

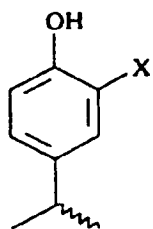
$R_5 = \text{benzotriazole.}$

The following BZT derivatives may serve as light stabilizers.



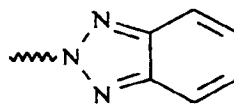
wherein:

$R =$



Hydroxyphenyl-
ethane (HPE) Branch

$X = H$ or



BZT

$n, m, \text{ and } o$ are 1-1000.

Physical Properties of PHS-BZT

Off-white, free flowing powder

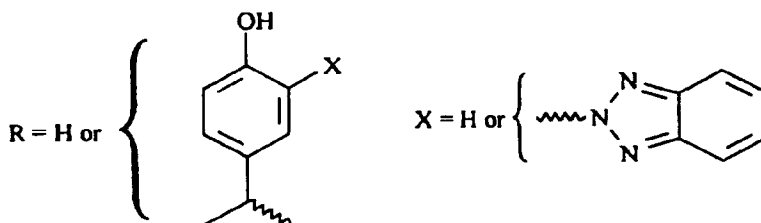
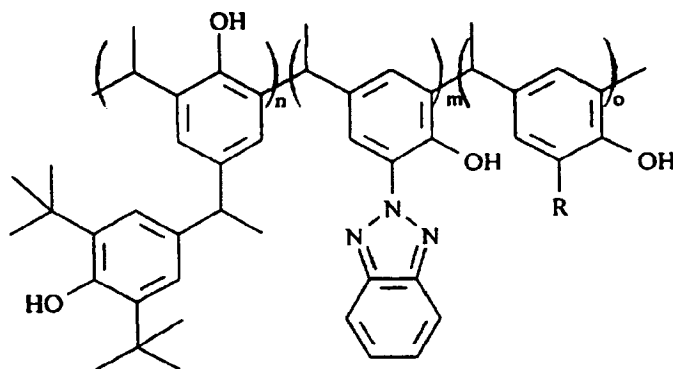
$M_w \sim 3000-6000$

Thermal Stability 1 % wt loss @ $> 200^\circ\text{C}$

5% wt loss @ $> 300^\circ\text{C}$

Decomposition onset $> 350^\circ\text{C}$

HPE-BZT concentration in PHS ~ 5 - 35%

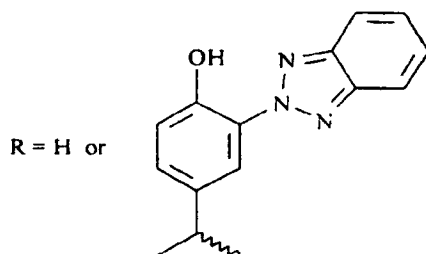
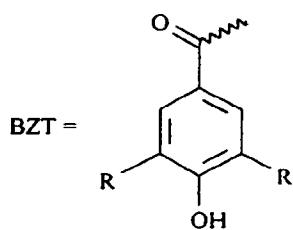
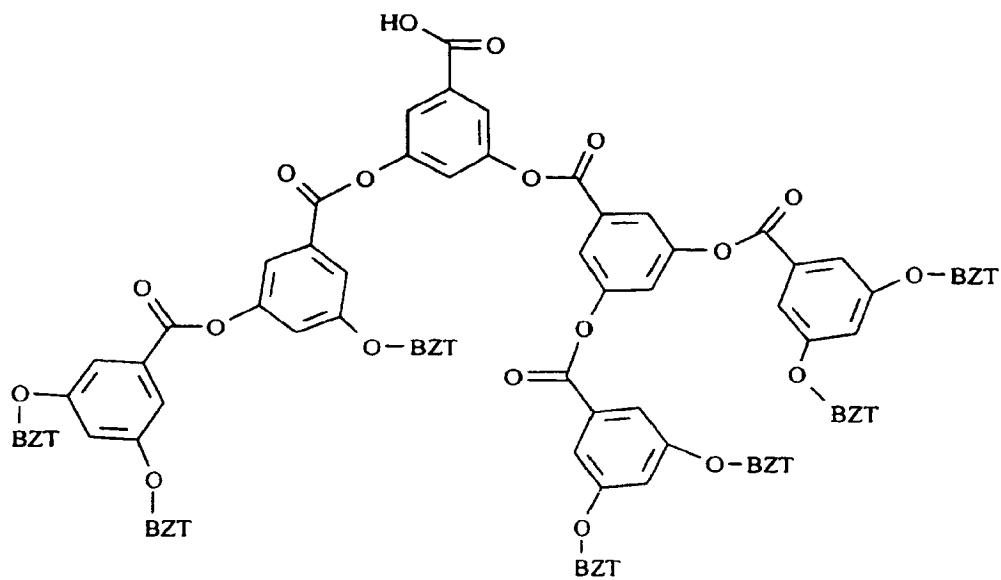


wherein n , m , and o are 1-1000;

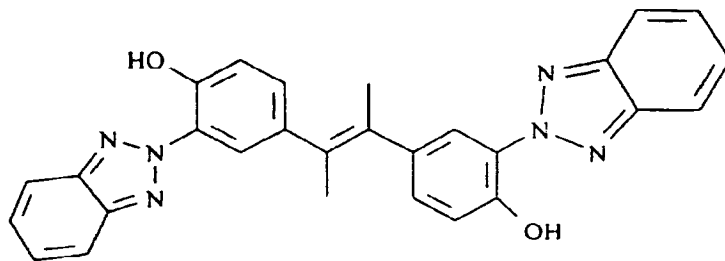
Hyperbranched Benzotriazole

Below is an example of a hyperbranched polymer that is functionalized with HPMC-BZT. Alkylation of phenolic end groups of a hyperbranched polymer with HPMC-BZT is accomplished using an acid catalyst (e.g. sulfuric, phosphoric, hydrochloric) in a solvent such as tetrahydrofuran. An advantage of a hyperbranched BZT is improved compatibility and solubility within polymer matrices where PHS-BZT may not blend well as an additive. Another advantage of the hyperbranched BZT's may be very low solution and melt viscosities. The low viscosities may be beneficial in high solids or powder coatings.

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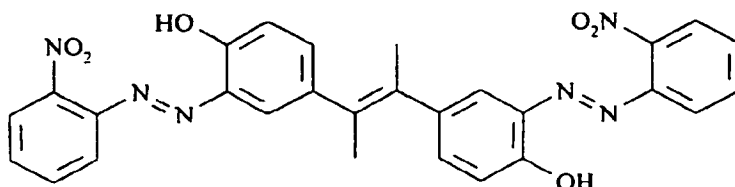


Preparation of bis-Benzotriazole from 4-Hydroxyacetophenone benzotriazole (bis-BZT):



The cis or trans bis benzotriazole can be synthesized using known carbonyl-coupling

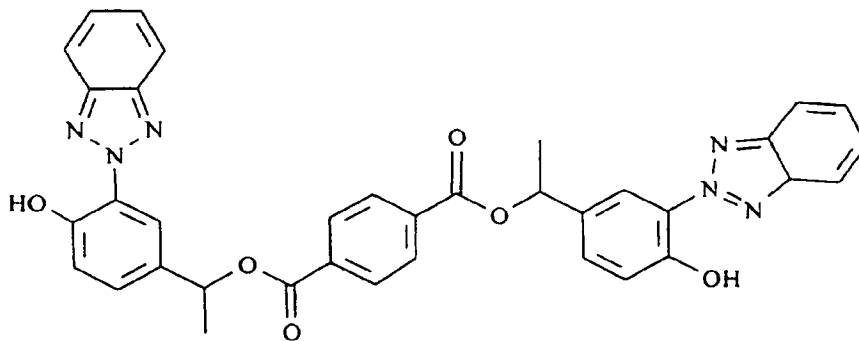
reagents such as low-valent Titanium (Reference: J. E. McMurry, Chem. Rev., 1989, 89, 1513-1524). An alternate route to synthesize this material is carbonyl coupling of 4-Hydroxyacetophenone, followed by azo coupling to the diazonium salt of o-nitroaniline:

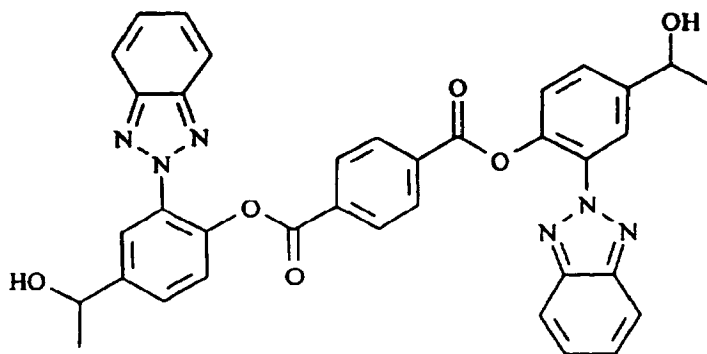


The resulting azo dye would then be reduced to the bis benzotriazole using either chemical or catalytic reduction described earlier. This UVLS offers both high temperature stability and a high concentration of the stabilizing functionality in the molecule.

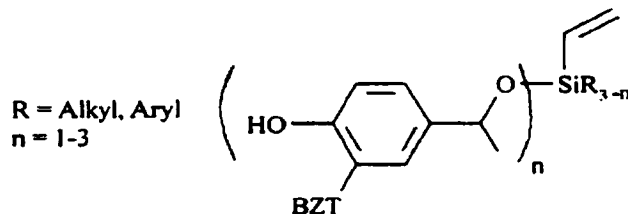
Bis Benzotriazoles from Terephthalic Acid Derivatives

Terephthalic acid and derivatives (i.e. terephthaloyl chloride) will react with HPMC-BZT to form esters of either the carbinol or phenol under varied reaction conditions. The carbinol substituted ester may be useful as a high molecular weight, thermally stable UVLS. Either compound may find further uses as metal complexation agents in photoresist applications.



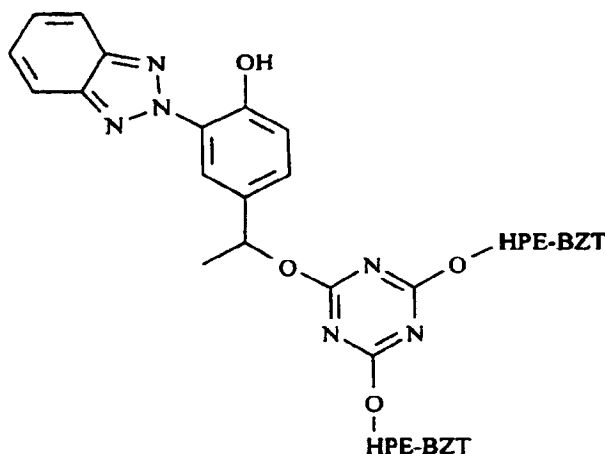


Preparation of Vinyl silyl ether BZT (VSE-BZT)

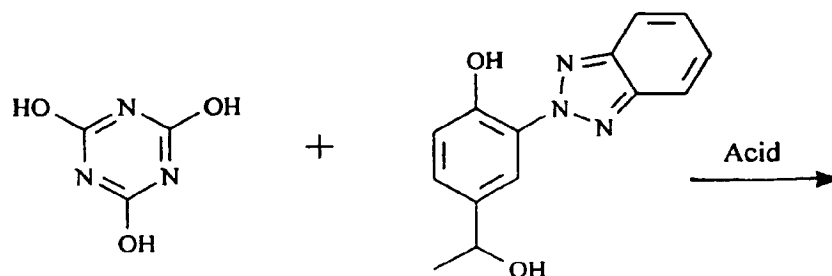


The vinyl silyl ether benzotriazole (VSE-BZT) can be synthesized under acidic or basic conditions from HPMC-BZT and vinylsilyl chlorides. VSE-BZT containing $n = 1-3$ stabilizing functional groups attached to the molecule would be polymerizable (i.e. polyolefins). Incorporation into the polymer backbone eliminates problems encountered with loss of additives from polymers during processing or use.

Preparation of Triazine Benzotriazole (TRZ-BZT)

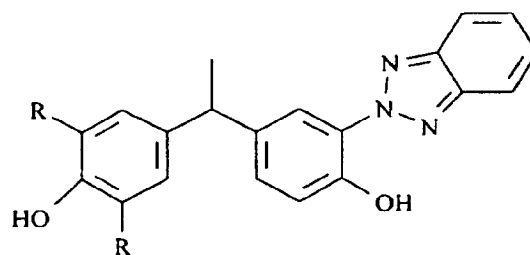


The triazine substituted benzotriazole can be prepared from the following reaction



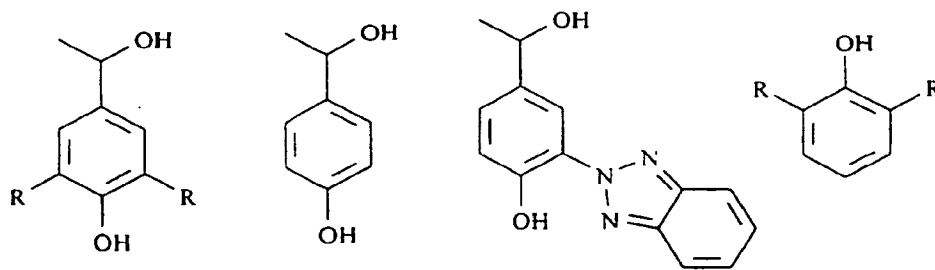
This molecule would offer thermal stability during polymer processing and use.

Preparation of Benzotriazole Anti-Oxidants (BZT-AO)



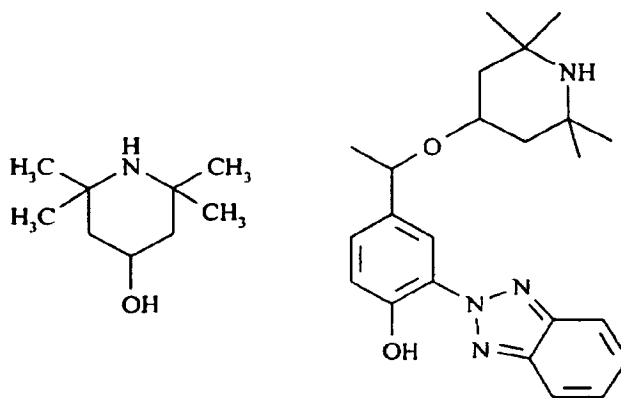
R = t-butyl, isopropyl

Hindered phenols can be alkylated with HPMC-BZT under acidic conditions to produce
 20 bifunctional UV light stabilizers that contain both anti-oxidant and benzotriazole functional
 groups. Incorporation of the hindered phenol functionality into the molecule adds a free-radical
 trap which will terminate radical chain reactions that can propagate oxidation of the polymer. (J.
 Pospisil, P. Klemchuk, Oxidation Inhibition in Organic Materials CRC Press, Vol. I. 1990,
 Raton, Fla., pp 66-8.) In addition, the following compounds can be used as monomers to form
 25 PHS-BZT with hindered phenol functionality built into the polymer.

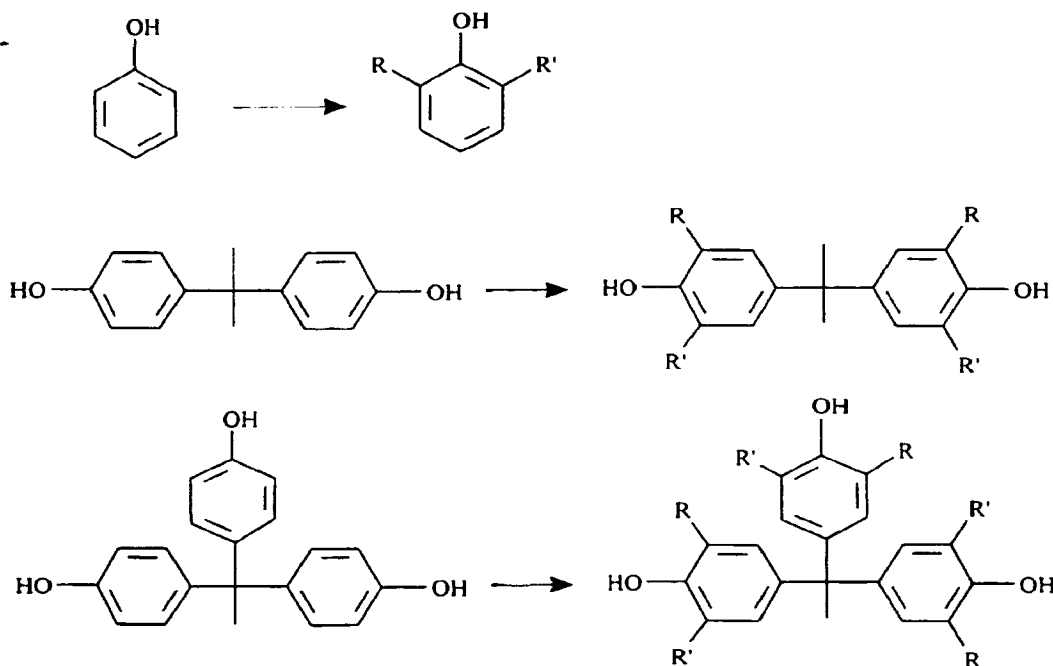


R = t-butyl, isopropyl

Similarly, hindered amines which also act as antioxidants, can be combined with benzotriazole functionality by acid catalyzed ether formation, or can be incorporated into a PHS polymer using conditions described previously.



Alkylation of Activated Phenols



Phenolic compounds can be alkylated with HPMC-BZT under acidic conditions giving typical UVLS shown. R and R' can be either hydrogen or Hydroxyphenylethane benzotriazole. Substitution of the phenolic rings may take place with one or two Hydroxyphenylethane benzotriazole groups.

Preparation of HPMC-BZT

NaBH₄ Reduction: 4-HAP BZT (90.7%, 30.01 g) was slurried in 150 g isopropanol, 150 g water, and 10.03 g 50% NaOH under a nitrogen purge. The solution was stirred at ambient temperature until most of the solids were dissolved. Sodium borohydride (12 wt % in 14 M NaOH, 10.01 g) was added slowly via an addition funnel. The solution was then heated to reflux. After 3 hours of stirring, an additional 46.0 g NaBH₄ solution was added in portions over several hours while stirring solution at reflux. Cooled to room temperature and acidified to pH 2 with 79.9 g of concentrated hydrochloric acid. The solution was chilled in an ice bath for several hours while stirring. The resulting solid product was filtered and washed with three portions of water (250 g). After drying 22.8 g HPMC-BZT (95.4%) was isolated giving an overall yield of 79%.

Preparations of PHS-BZT

Graft copolymer: PHS-N (0.48 g, Mw = 5600) and HPMC-BZT (91.9%, 0.14 g) were dissolved in 25 mL glacial acetic acid. Following the addition of 3 drops of concentrated sulfuric acid, the solution was stirred at room temperature for 3 days. The solution was added dropwise to 300 mL water to precipitate the polymer. The polymer was then filtered and dried overnight in a warm (<50 °C) oven with a nitrogen purge, yielding an off-white powder. Reaction occurred at the carbinol hydroxy group, while the phenol did not react. This result was determined from UV-VIS absorption spectra where λ_{max} observed at 354 nm will blue shift if hydrogen bonding between the ortho hydroxy and benzotriazole group is disrupted. No shift in λ_{max} was observed when comparing HPMC-BZT to PHS-BZT. Mw obtained by GPC was 6077 with a polydispersity of 1.61.

PHS-BZT Co-polymer (HPMC BZT + 2-HPMC): Combined 2-HPMC (90%, 5.35 g), HPMC-BZT (91.9%, 1.03 g) and 25 mL glacial acetic acid, then added 3 drops concentrated sulfuric acid. After two days, the solution was added dropwise to water to precipitate the polymer. After the slurry was stirred one hour, the polymer was filtered, washed with water then toluene, and dried. Based on UV-Vis absorption spectra, the HPMC-BZT was successfully incorporated into the polymer through reaction at the carbinol.

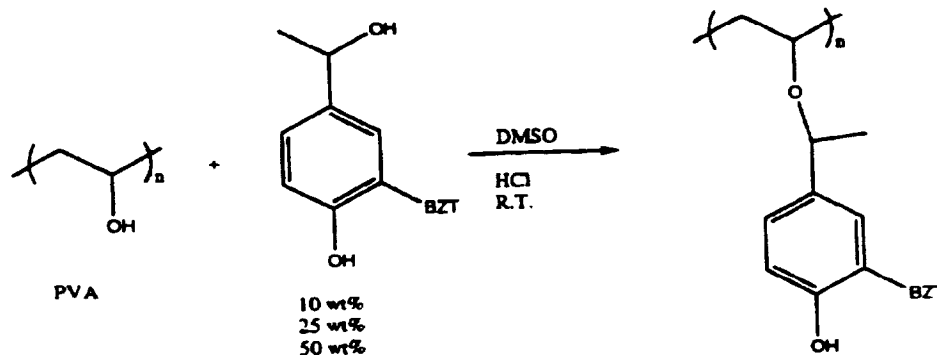
PHS-BZT Co-polymer (HPMC-BZT + 4-HPMC): Combined 5.41 g HPMC-BZT (99.8%) and 20.21 g HPMC (97.7%) with 350 mL glacial acetic acid. The slurry was stirred until most of the starting material dissolved. Concentrated sulfuric acid (2 drops) was added and

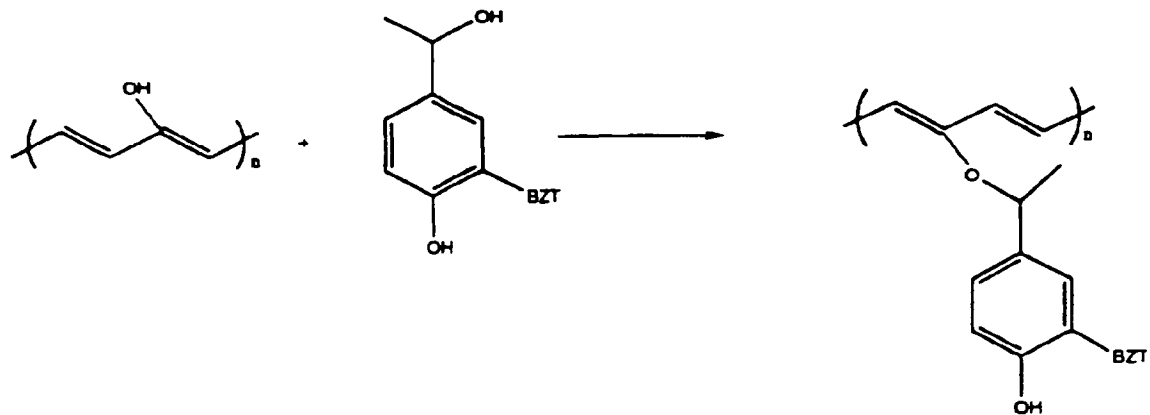
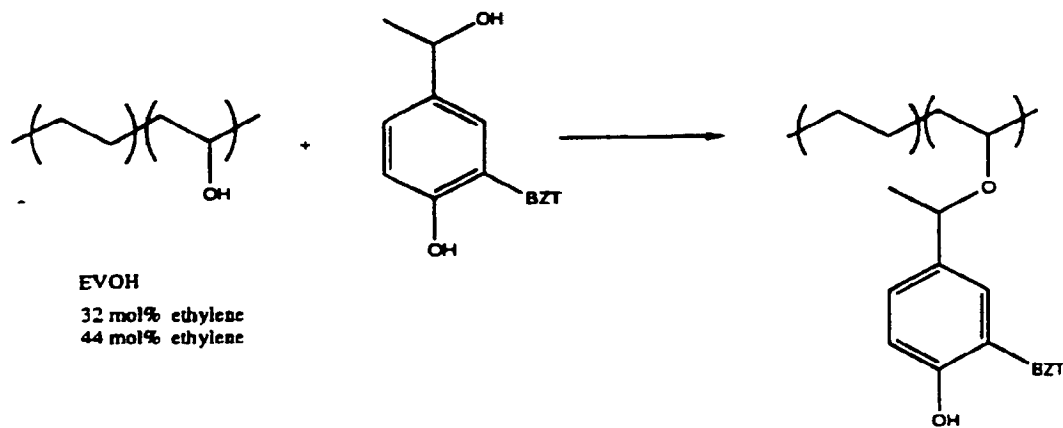
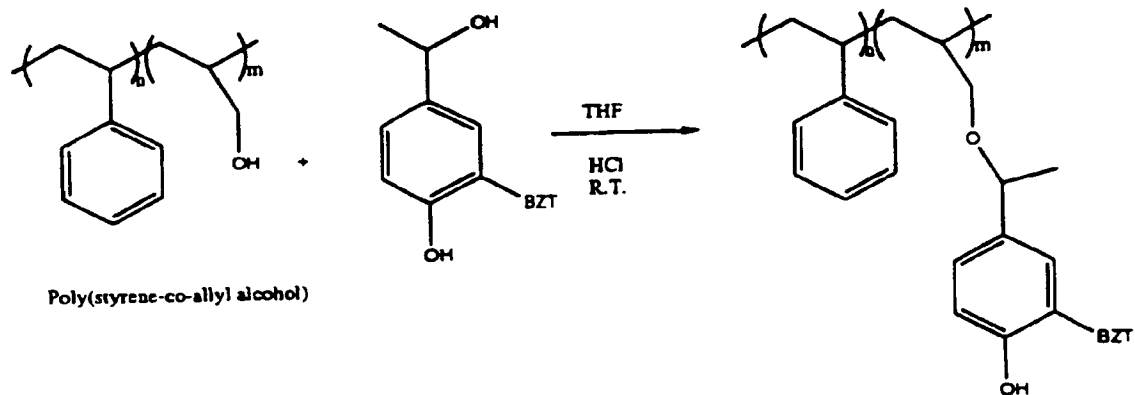
the solution was then stirred at room temperature two days. The solution was added dropwise to 1200 mL water while stirring. The polymer was filtered after stirring 1 hour, washed with 3 portions (200 mL) water, followed by 2 portions (250 mL) toluene. After drying in a vacuum oven overnight, 26.30 g off-white powder were collected. UV-Vis absorption spectral results were identical to those observed with the graft and 2-HPMC co-polymer. No blue shift in λ_{\max} was observed. GPC analysis gave a molecular weight (Mw) of 3619 with a polydispersity of 1.52. The structure was confirmed by NMR.

PHS-BZT Anti-Oxidant Co-polymer (HPMC BZT + HMPC + 2,6-di-t-butylphenol):

Combined HPMC-BZT (95.2%, about 4.73 g), (97.73%, about 20.94 g), 2,6-di-t-butylphenol (99%, about 3.46 g) and 180 g glacial acetic acid. Added 1.93 g concentrated sulfuric acid and stirred at room temperature 70 hours. The acetic acid solution was added dropwise to 1400 mL water to precipitate the polymer. The polymer was filtered, washed with 3 portions of 500 mL water and dried. Based on UV-VIS absorpton analysis the benzotriazole moiety was incorporated at 12.4 wt %. From NMR data, the hindered phenol was incorporated into the polymer backbone at 12 mole %. The polymer was found to have a decomposition onset temperature of 353 °C with 5% wt loss at >250 °C. Based on GPC, the polymer had an Mw of 3284 with a polydispersity of 1.88.

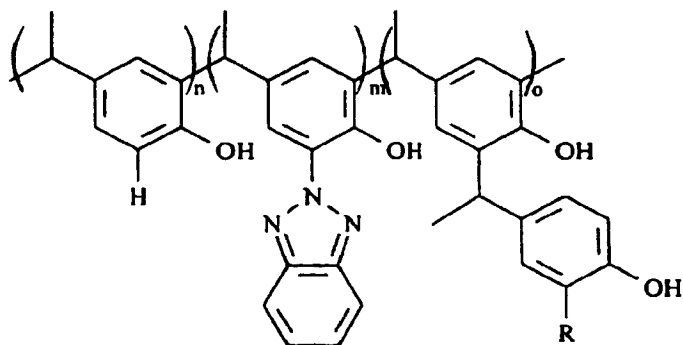
Additional Reaction Schemes for Preparation of PHS-BZT Derivatives:





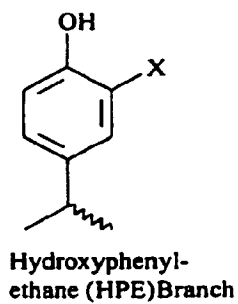
CLAIMS

1. A compound whose derivatives may serve as stabilizers:

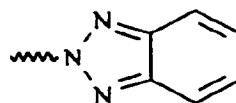


wherein:

R =



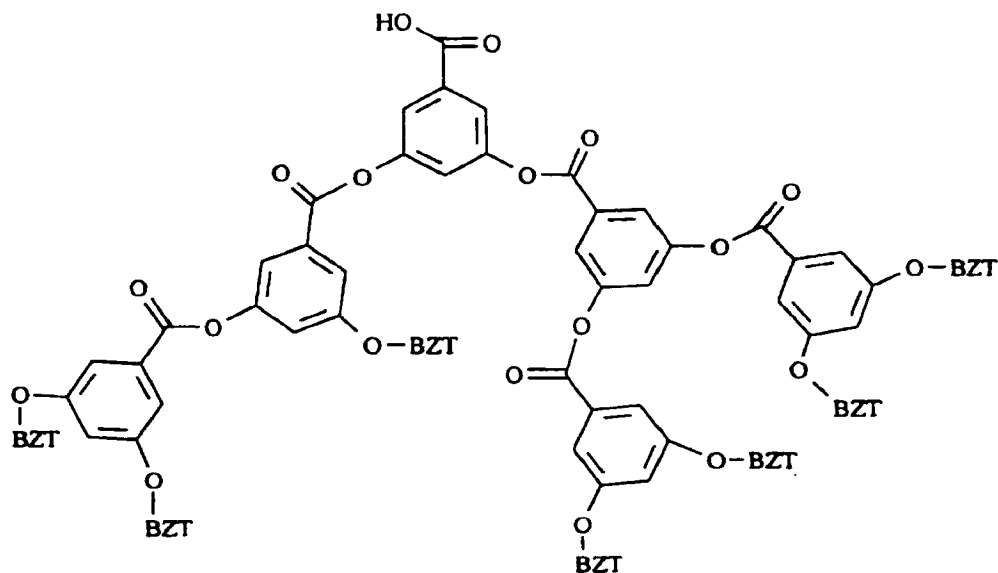
X = H or



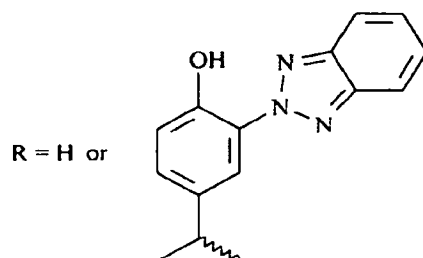
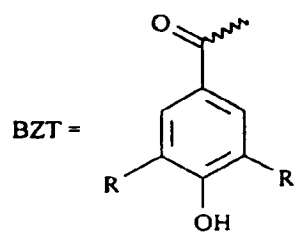
BZT

n, m, and o are 1-1000.

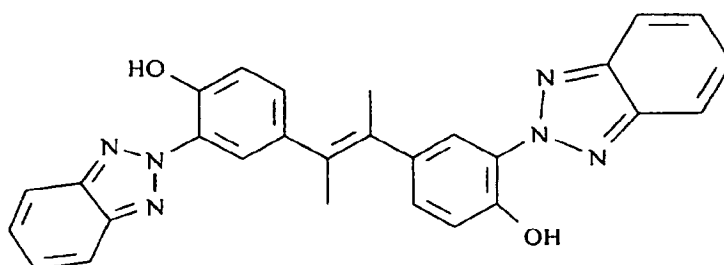
2. A compound having the formula



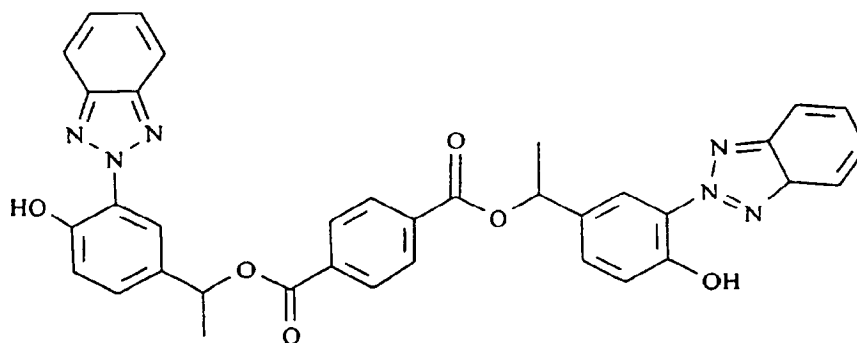
21



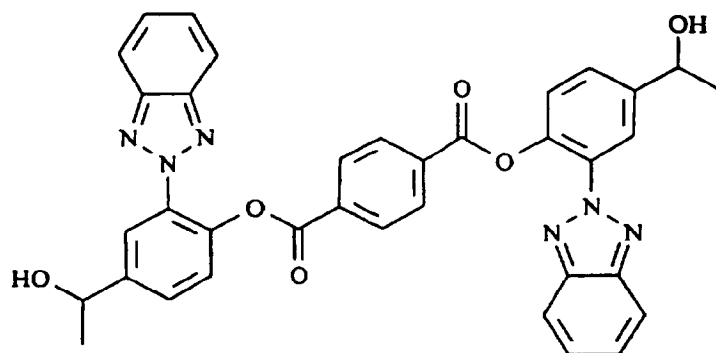
3. A compound having the formula



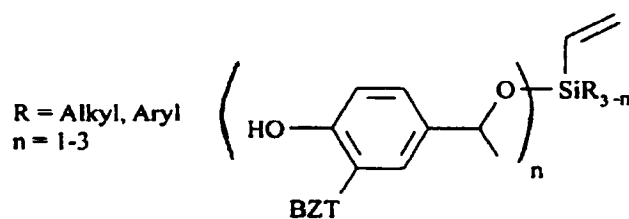
4. A compound having the formula



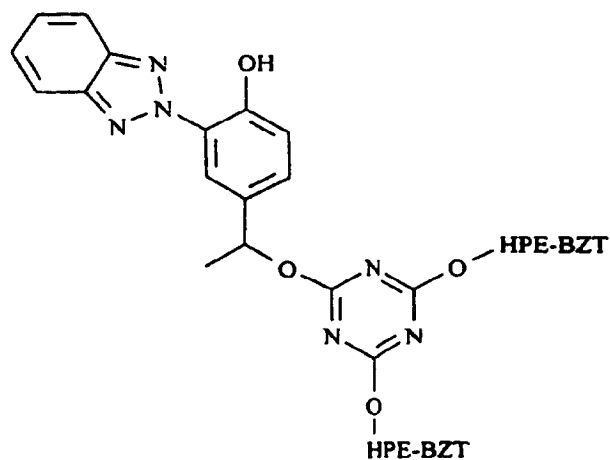
5. A compound having the formula



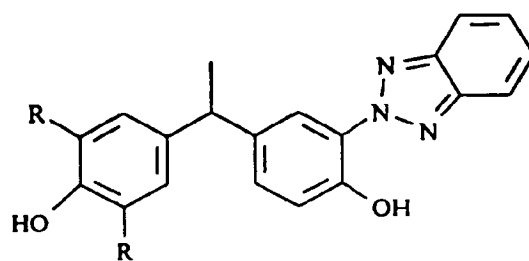
6. A compound having the formula



7. A compound having the formula

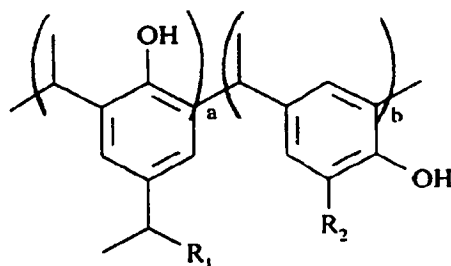


8. A compound having the formula

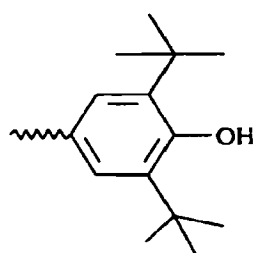


R = t-butyl, isopropyl

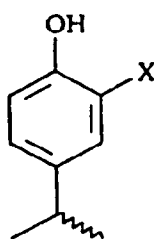
9. A compound having the formula



wherein R₁ is

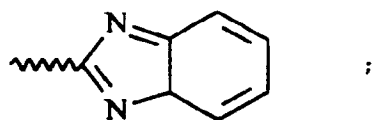


R₂ is H,



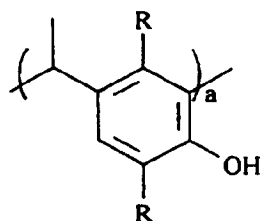
24

X is H,



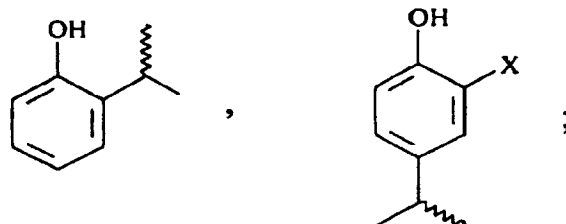
5 a is 1-1000; and b is 1-1000.

10. A polymer compound having the formula

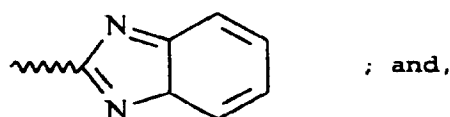


wherein:

R is H,

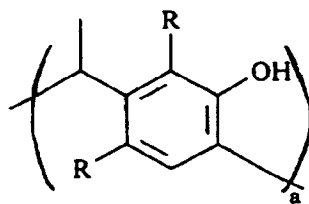


X is H,



a = 1-2000.

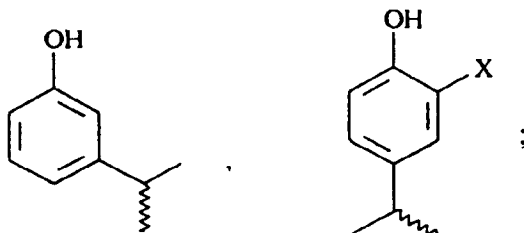
11. A compound having the formula



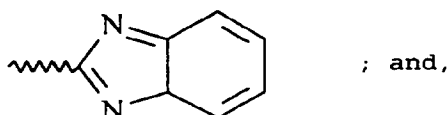
wherein:

25

R is H,



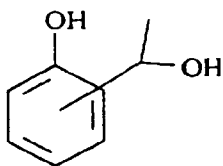
X is H,



a = 1 - 2000.

12. A process to prepare PHS-BZT comprising contacting under suitable reaction conditions

a)



and

b)

BZT.

13. A process to prepare a copolymer of HPMC and HPMC-BZT comprising contacting under suitable reaction conditions HPMC and HPMC-BZT.

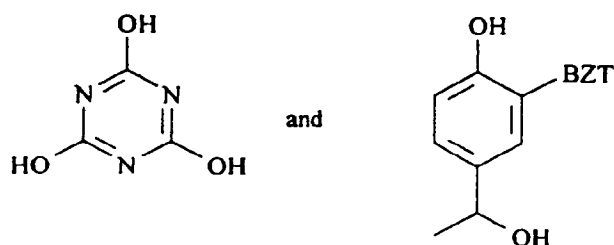
14. A copolymer of HPMC and HPMC-BZT.

15. The copolymer of claim 14 wherein the HPMC is ortho substituted.

16. The copolymer of claim 14 wherein the HPMC is para substituted.

17. A graft polymer comprising PHS and HPMC-BZT.

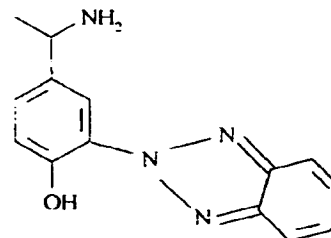
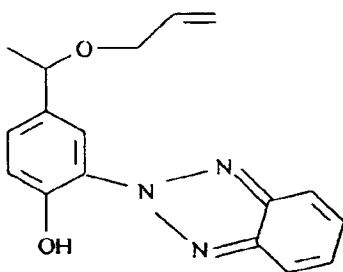
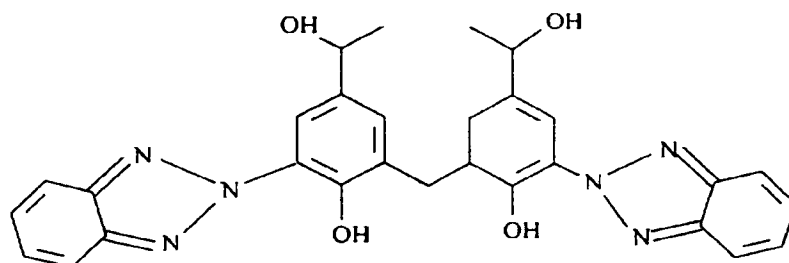
18. A process for preparing TRZ-BZT comprising contacting under suitable reaction conditions



19. A process to prepare a bifunctional UV light stabilizer comprising contacting under suitable reaction conditions, a hindered phenol and PHS-BZT.

20. A process to prepare a UVLS comprising contacting under suitable reaction conditions a phenolic compound and HPMC-BZT.

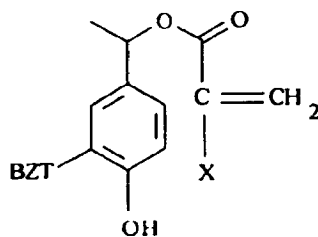
21. A compound



22. A process for preparing derivatives of HPMC-BZT comprising contacting under suitable reaction conditions HPMC-BZT and at least one of the following compounds

27

a)

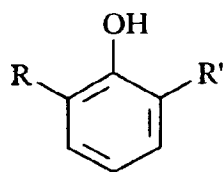


b) allyl ether

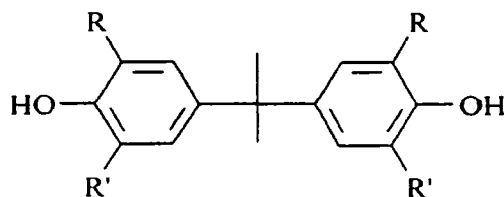
c) α -amino ethyl phenol

d) vinyl silyl ether

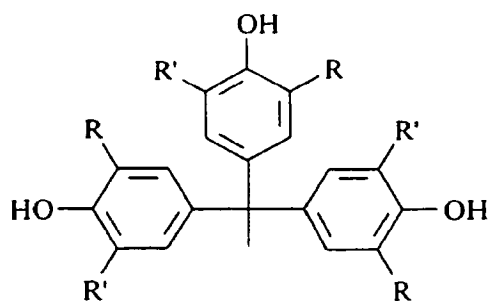
e)



f)



g)



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